Low Damage Photoresist Material Modification with Electron Beam-Generated Plasmas

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Abstract

The Naval Research Laboratory has developed a materials processing system based on plasmas produced by high-energy (≈ 2 keV) electron beams. These plasmas have numerous properties that allow operating regimes not accessible in systems using conventional plasma sources. The system is being used to examine the etching behavior of 193 nm and 248 nm photoresist material in argon plasmas. The initial results of this work are presented.

Keywords: Plasma Source, Electron Beam, Etching, Photoresist

1. Introduction

The Naval Research Laboratory has developed a materials processing system based on electron beam-generated plasmas for use in a variety of processing applications [1]. The systems utilizes a magnetically collimated, sheet of high-energy (≈ 2 keV) electrons to produce a planar plasma. The resultant plasma has unique characteristics when compared to conventional low-pressure plasma sources. When multi-kilovolt electrons pass through a gas, ionization is the dominant mechanism with the cross-sections being similar for most gases. Thus, little energy is consumed by non-ionizing, inelastic collisions and species generation can be regulated by adjusting the background gas concentrations. This in contrast to conventional discharges where the dominant inelastic collisions consume most of the delivered energy and ion production favors the species with the lowest ionization potential.

Also, in conventional discharges, the boundaries of the ionization region are not well defined and can vary greatly with gas pressure and composition or chamber geometry. In electron beam-produced plasmas, the ionization region is limited to the beam volume, which is well defined and uniform when the beam is magnetically confined. Outside the beam channel, the plasma density and ion composition are altered by ion-electron, ion-neutral, and ion-ion reactions and so electrodes (or substrates) can be independently positioned to take advantage of changes in the outwardly diffusing flux of ions and radicals.

Perhaps the most notable difference of electron beam-generated plasmas, is a low electron temperature. Conventional plasma discharges rely on externally applied electric fields to raise the plasma electron temperature so that a fraction of those electrons are energetic enough to ionize the gas and sustain the plasma. Because the electron beam ionizes the gas, no heating of the plasma electrons is required and they are quickly cooled by elastic and inelastic collisions. The resulting plasma electron temperatures are found to be 1.0 eV or lower [2], depending on the background gas. The temperature in molecular gas backgrounds tends to be lower than in noble gases due to the availability of excitation states that extend down to near zero energies. Since the electron temperature determines the plasma potential, ions incident to unbiased surfaces will also exhibit low energies [3], typically below 5 eV.

It is with these attributes in mind that electron beam generated plasmas are being used to investigate the etching behavior of 193 nm and 248 nm photoresist materials. The 193 nm photoresist material is, by necessity, thinner and based on a different polymeric structure than 248 nm photoresist material but has been found to be less robust than 248 nm photoresist material when subject to conventional argon and C_4F_8 based discharges [4]. In this work, we present and discuss experimental characterizations of electron beam-generated plasmas produced in argon, which are used to etch 193 nm and 248 nm photoresist material. The etch behavior of the photoresist materials will also be discussed.

2. Experimental

A number of systems are currently in use for plasma diagnostics and materials processing. While the chamber geometries vary, all systems operate in a similar fashion and consist of a few common components, which are shown in Fig. 1. A sheet-like beam of energetic electrons is produced by pulsing a linear hollow cathode to -2 kilovolts for a fixed pulse width and duty factor. The emergent beam passes through a slot in a grounded anode and is then terminated at a second grounded anode located further downstream. The electron beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (beam thickness and width) and the anode-to-anode distance (beam length). For these applications, the range of a 2 keV electron beam is much larger than the anode-to-anode length. A set of external magnetic field coils produce a coaxial magnetic field of 150 Gauss or higher. Magnetic fields of this magnitude keep the expansion of a 2 keV electron beam in 50 mTorr to less than 0.5 cm at a distance of about 50 cm [5].

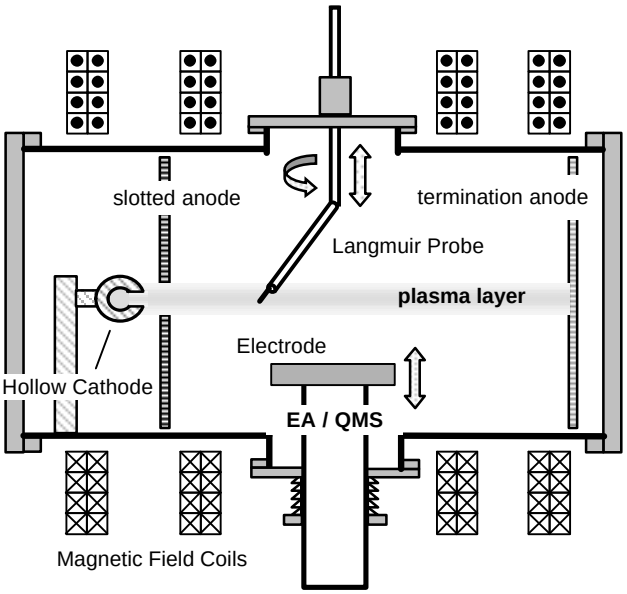

Fig. 1 The experimental apparatus used for plasma characterization.

Plasma Diagnostics

The experimental apparatus has been discussed previously [6] and is shown in the schematic of Fig. 1. The source volume in this system measures approximately 1 cm thick by 25 cm wide by 43 cm long. A dual energy analyzer/mass spectrometer (Hiden EQP 300 Plasma Probe) was used to measure mass-resolved ion energy distributions and ion fluxes sampled through a 20 μm diameter aperture located in the center of a grounded 5.7 cm diameter stainless steel electrode. Because the system was pulsed, all data acquisition was time resolved and the gating techniques have been described elsewhere [6].

The plasma electron temperature and plasma density, were determined using a Langmuir probe that was mounted on a multi-motion feedthrough and constantly heated with an internal resistive element to reduce surface contaminants. The electron temperature and plasma density were derived from a best fit of the I-V trace to a Maxwellian electron energy distribution using time-resolved probe techniques that have also been described elsewhere [7].

Etching Experiments

Details of the electron beam source and reactor used for the etching experiments can be found in [8] and the approach to system operation for etching applications have been previously described [9]. The system was similar to the experimental configuration of Fig. 1 except all diagnostics are absent and the ground electrode was replaced by a biasable stage upon which the photoresist material is mounted. Rf power was applied to the stage through a matchbox by an rf amplifier driven at 13.56 MHz. The rf signal was synchronized to the electron beam pulse so that the rf power was well coupled to the electron beam–produced plasma, thereby minimizing any undesirable rf discharge effects. Stage bias and currents were measured by an oscilloscope probe and current transformer on the atmosphere side of the electrical feedthrough. Forward and reflected powers were determined using an inline directional coupler.

1-2 cm^2 samples of blanket 248 nm (1000 nm thick) and 193 nm (400 nm thick) photoresist films on silicon substrates were adhered to the stage with silver print epoxy, placed in vacuo, and the chamber was evacuated to a pressure of at least ~10^{-5} Torr. The samples were then subjected to plasmas produced in 50-60 mTorr of high-purity argon (50 sccm) with the cathode operating at –2 kV for a range of pulse widths and duty factors in a 150

Gauss magnetic field. The samples were positioned 2.5 cm from the electron beam axis. Post-treatment, the systems was again evacuated to 10^{-5} Torr and then brought to atmosphere with nitrogen. *Ex situ* sample analysis included ellipsometry to determine etch depths and changes in refractive index, contact angle measurements of water drops on the surface, and x-ray photoelectron spectroscopy (XPS) to assess the surface chemical structure.

3. Results and Discussion

Plasma Diagnostics

Plasma diagnostics have been carried out on plasmas produced in 50 mTorr of argon using an electron beam produced by pulsing the hollow cathode to –2 kV for 6 ms at a 10% duty factor. Shown in Fig. 2 are Ar^+ ion energy distributions measured at a grounded electrode positioned 2.5 cm from the electron beam axis. One distribution (open circles) was acquired during a gate extending over nearly the entire pulse period. The other distribution (solid circles) was limited to the last millisecond of the electron beam pulse. The distributions indicate a low incident ion energy but clearly differ in breadth and shape. Complimentary probe data, measured on the beam axis and directly above the electrode, is shown in Fig. 3a. During the course of one period, the electron temperature was characterized by larger values just after the plasma was initiated, followed by a period of near steady-state values, and then a collapse in the afterglow. The electron temperature determines the plasma potential, which then sets the energy range of ions incident to the electrode from the plasmas. It's not surprising then, that the ion energy distribution acquired over the entire period (open circles in Fig. 1) was characterized by a broader energy distribution than the distribution measured when the electron temperature was nearly constant (solid circles in Fig. 1).

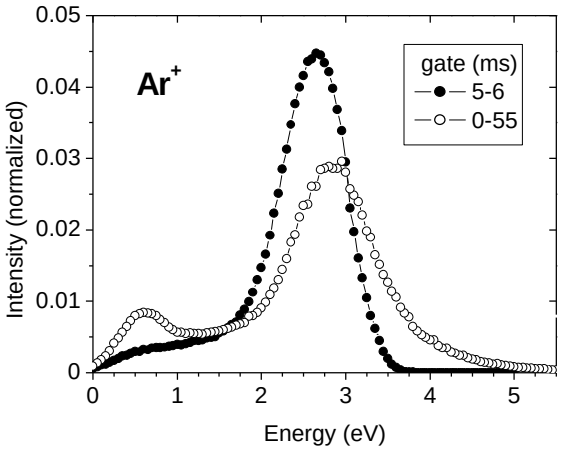

Fig. 2 Ar^+ ion energy distributions measured at a grounded electrode.

Also shown in Fig. 3 are the on axis plasma density and the total Ar^+ ion flux at the electrode. From these plots, it can be seen that the density and flux are reasonably well correlated. The slight temporal difference in relative intensities is expected since the density was measured on-axis and the flux was measured 2.5 cm from the electron beam axis.

A time-dependent ion flux adds a degree of freedom when considering possible surface effects in materials processing applications. A more detailed discussion of the temporal dependencies in argon plasmas can be found in [6]. Important to the etching applications is that the ion flux to the grounded electrode was characterized by low ion energies (< 5 eV). This provides the possibility of exploring the etch response at or near sputtering threshold energies in a high flux, low pressure environment. To explore higher ion energies, an applied bias is required. Previous studies [10] showed this can

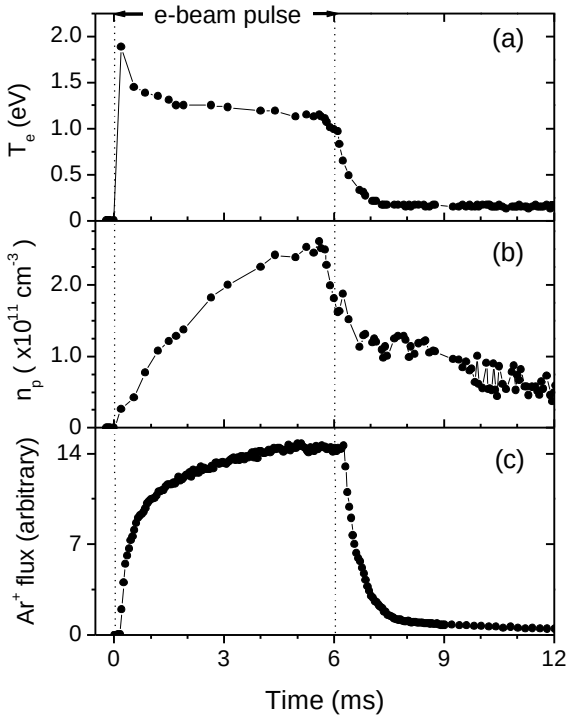

Fig. 3 (a) Electron temperature and (b) plasma density measured on the electron beam axis and (c) the Ar^+ ion flux measured at a grounded electrode located 2.5 cm from the beam axis.

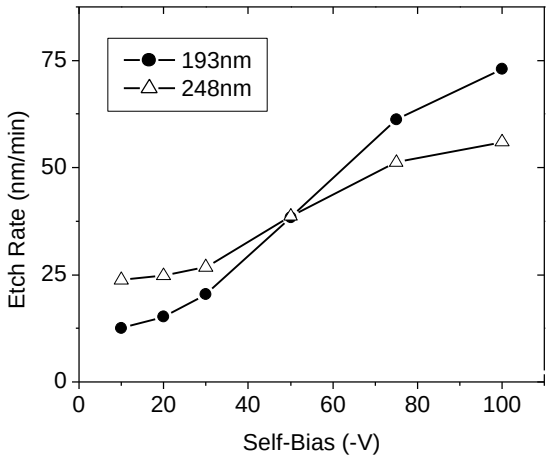

Fig. 4 Photoresist etch rate in electron beam-generated plasmas produced in argon.

be accomplished without altering the electron temperature, thereby providing a narrow energy distribution about a selected energy.

Photoresist Etching

Our work to date has focused on etch rate and limited surface characterization. The etch rate as a function of substrate bias and plasma duty factor for both 248 nm and 193 nm photoresist material are shown in Figs. 4 and 5. The substrate bias is the self-bias induced by the applied rf power, measured by the voltage probe. The experiments of Fig. 4 were carried out using a 4 ms pulse width and a 20% duty factor for a fixed exposure time of 2.5 min. These results are interesting in that the etch rate for the 248 nm photoresist is greater than the rate for the less stable 198 nm photoresist at low self-biases. For self-biases above –50 V the opposite was true, which is consistent with the results found using a transformer coupled plasma source operating at a self-bias of –100 V [4]. The finding of a larger etch rate for the 248 nm photoresist, which is based on a more stable aromatic backbone, compared to the 193 nm material at the low self-bias voltages is surprising. The reason for this behavior is currently being investigated.

The results of Fig. 5 indicate no strong dependence on the duty factor for a fixed pulse width (10 ms) and total exposure time (26 s), using a –10 V self-bias. Note that the relative etch depths shown were normalized by the forward rf power, to eliminate any difference in plasma production caused by operating at widely varying duty factors. Note however, that the slight increase in the etch depth of the 193 nm material with increasing off time suggests the initiation of reactions producing volatile products by the plasma exposure. These reactions, once initiated, will continue without additional particle bombardment and are consistent with a reduced chemical stability of the 193 nm material.

We also have performed ellipsometry, contact angle, and x-ray photoemission studies of plasma-treated photoresist materials. These show increasing surface roughness of both photoresist materials and changes in chemical structure of the 193 nm photoresist material after processing. Results of these studies will be reported in a future publication.

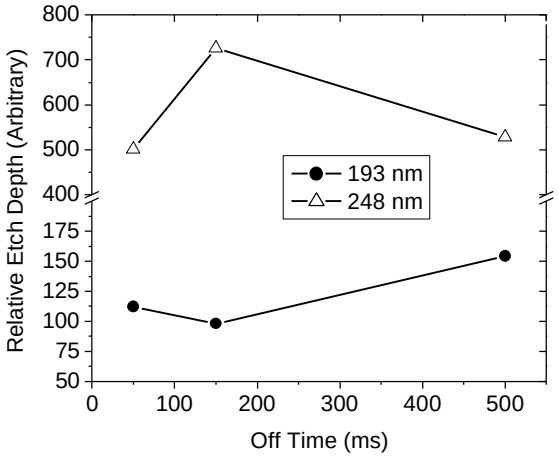

Fig. 5 Photoresist etch rate as function of plasma duty cycle. Off time indicates time between pulses.

4. Summary

Pulsed, electron beam-generated plasmas produced in argon were used to study the etch behavior of 193 nm and 248 nm photoresist material. Plasma diagnostics show the electron temperature, plasma density, and incident Ar^+ have clear time dependencies but in general, the plasmas are characterized by low electron temperatures (1 eV), high densities ($>10^{11}$ cm^3), and low ion energies (< 5 eV) at adjacent grounded electrodes. The etch rates for the photoresist materials were determined for a range of processing conditions. Interestingly, the etch rate of 193 nm photoresist was found to be lower than the etch rate of 248 nm photoresist for low substrate biases (incident ion energies below 50 eV) but was consistent with previous findings at higher bias conditions. Additional work is planned to further explore these behaviors.

5. Acknowledgments

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